

## PATENT ABSTRACTS OF JAPAN

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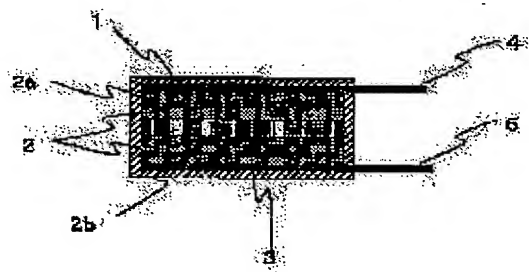
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## 54) LITHIUM BATTERY

## 57)Abstract:

**PROBLEM TO BE SOLVED:** To provide similar electrochemical characteristics to a case using organic electrolytic solution by arranging a solid electrolytic layer comprising solid electrolytic powders, polyvinylidene fluoride, and N-methylpyrrolidone between a pair of electrodes.

**SOLUTION:** A solid electrolytic layer 3 is arranged between a pair of electrodes 2. The positive electrode 2a and the negative electrode 2b are composed of respective active material powders and powders of a same material as the solid electrolytic layer 3. From the viewpoint of ionic conductivity, the solid electrolytic powders mixed in the solid electrolytic layer 3, the positive electrode 2a, and the negative electrode 2b are preferably oxide crystallized glass. The positive electrode 2a and the negative electrode 2b are so mixed that the volume ratio of the active material powders to the solid electrolytic powders becomes 50:50-97:3. The solid electrolytic layer 3 is so mixed that the weight ratio of the solid electrolytic powders to polyvinylidene fluoride becomes 97:25-25:3, N-methylpyrrolidone is added thereto and slurried, and the viscosity is adjusted.



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CLAIMS

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## Claim(s)]

Claim 1]A lithium cell which allocates a solid electrolyte layer which comprises this solid electrolyte powder, polyvinylidene fluoride, and N-methyl pyrrolidone in inter-electrode [ of a couple which comprises electrode active material powder, solid electrolyte powder, a conducting agent and polyvinylidene fluoride ].

Claim 2]The lithium cell according to claim 1, wherein said solid electrolyte powder is oxide stock glass ceramics which have lithium ion conductivity.

Claim 3]Said electrode active material A lithium manganese multiple oxide, manganese dioxide, lithium nickel complex oxide, A lithium cobalt multiple oxide, a lithium nickel cobalt multiple oxide, The lithium cell according to claim 1 or 2 comprising any one sort of a lithium vanadium multiple oxide, a lithium titanium multiple oxide, titanium oxide, niobium oxide, vanadium oxide, tungstic oxide, or those derivatives, or two or more sorts.

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## DETAILED DESCRIPTION

## Detailed Description of the Invention]

0001]

Field of the Invention]Especially this invention relates to the lithium cell which improved the electrolyte about a lithium cell.

0002]

Description of the Prior Art]The energy density of a lithium ion battery is high, and there is little self-discharge, and it is widely used for a cellular phone, a notebook computer, etc. taking advantage of the characteristic of being able to respond to a mothball. Cobalt acid lithium ( $\text{LiCoO}_2$ ) and manganic acid lithium ( $\text{LiMn}_2\text{O}_4$ ) are generally used as positive active material, and, as for these lithium ion batteries, carbon materials, such as corks and carbon fiber, are used for negative electrode active material.

0003]Generally structure of a lithium ion battery is made into aluminum foil or copper foil with \*\* with above-mentioned positive active material and negative electrode active material, conducting agents, such as acetylene black and black lead, and binders, such as polyvinylidene fluoride (PVdF) and polytetrafluoroethylene (PTFE), It was rolled round by spiral shape via the separator which are a product made from polypropylene, the products made from polyethylene, or those combination, and was inserted into the battery can, and the organic system electrolysis solution was poured in further and it had obturated.

0004]The components of these organic system electrolysis solution are a solvent and electrolyte salt, and as a solvent Propylene carbonate (PC), Dimethoxyethane (DME), ethylene carbonate (EC), dimethyl carbonate (DMC), it is used, where diethyl carbonate (DEC) was independent or is mixed, As electrolyte salt,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ , etc. are used.

0005]With the thin shape of various electronic applied machines and the demand of a miniaturization which are represented by portable information-and-telecommunications terminals, such as a cellular phone and a notebook computer, it replaces with the above organic system electrolysis solutions, and the lithium cell using a polymer electrolyte attracts attention in recent years.

0006]A polymer electrolyte is the admixture of the polymers and electrolyte salt which have a donor type polar group represented by polyethylene oxide (PEO) and polypropylene oxide (PPO).

An electrolyte layer can be thin-film-ized and improvement in an energy density is expected.

Or since there are no worries about a liquid spill and corrosion and a volatile solvent is not used, that there is little danger of explosion or ignition etc. can desire improvement in a battery characteristic and safety.

0007]However, the above-mentioned polymer electrolyte has the problem that the degree of ion \*\*\*\* is low as compared with an organic system electrolysis solution, and since the gel electrolyte with which the polymer electrolyte was made to mix an organic system electrolysis solution has the ionic conductivity which is equal to an organic system electrolysis solution, development is performed briskly.

0008]When such a gel electrolyte is used, it is difficult to keep ideal electric contact of a solid electrolyte layer and an electrode layer, for example, in JP,7-326383,A. Laminate what mixed the solvent with electrolyte salt to the high molecular compound, and polymerized the monomer composition to a positive active material layer, and a positive active material layer is impregnated with some monomer compositions, By polymerizing, sticking the monomer composition with which the positive active material layer was impregnated, and the monomer composition laminated on the surface of positive active material to a positive active material layer, and producing a solid polymer electrolyte to a laminating condition, fully sticking a positive active material layer and a solid polymer electrolyte is proposed.

0009]In JP,8-111233,A, reducing resistance of the interface of the anode and solid electrolyte in which the both ends or end of the main chain of polyether, a polythioether, or polyacrylate carried out the chemical bond to the positive-electrode-oxidation thing surface, and the interfacial resistance of positive-active-material particles is proposed.

0010]By inserting the mixture of the organic compound, the organic solvent, and lithium salt which have a functional group which can polymerize in JP,8-315855,A between two electrodes, and completing a polymerization after that, Generation of the interface between an electrolyte and an electrode is prevented and preventing exfoliation with a solid electrolyte and an electrode etc. is proposed.

0011]In JP,3-37971,A, in an organic high polymer solid electrolyte, LiI, Distribute inorganic solid electrolytes, such as Li-beta-aluminum  $2O_3$ ,  $Li_3N$ , and LiI-aluminum  $2O_3$ , and ionic conductivity is raised, and it has pliability and the thin cell with high reliability with withstand voltage is proposed.

0012]In the polymer electrolyte which mixed electrolyte salt with the solute in JP,9-50816,A, While mechanical properties and processability are excellent by distributing metal carbonation things, such as  $Li_2CO_3$ ,  $CoCO_3$ ,  $NiCO_3$ , and  $MgCO_3$ , the high compound solid electrolyte of the chemical stability in an interface with a negative electrode is proposed.

0013]However, in these methods, there is a problem that electrolytic lithium ion conductivity will still become low, and current density will become small, and many the organic solvents and lithium salt which are main lithium ion conductors needed to be included.

0014]In this invention, it is made in view of the above conventional problems, and the interfacial resistance of an electrode, a solid electrolyte layer and an electrode active material particle, solid electrolyte particles, electrode active material particles, and solid electrolyte particles is reduced.

Therefore, examination of various high molecular compounds and a solvent was performed for the purpose of finding out the electrochemical characteristics which are equal to an organic system electrolysis solution.

0015]As a result, it differs from the gel electrolyte with which the conventional polymer electrolyte was made to mix an organic system electrolysis solution, If the combination of N-methyl pyrrolidone (NMP), the polyvinylidene fluoride (PVdF), and the solid electrolyte it was presupposed that electrolyte salt was not added and were not functioned as a solute of an electrolysis solution is used for an electrolyte, It found out acquiring electrochemical characteristics equivalent to the lithium cell using an organic system electrolysis solution, and resulted in this invention.

0016]

Means for Solving the Problem]In a lithium cell of this invention, a solid electrolyte layer which comprises this solid electrolyte powder, polyvinylidene fluoride, and N-methyl pyrrolidone is allocated in inter-electrode [ of a couple which comprises electrode active material powder solid electrolyte powder, a conducting agent, and polyvinylidene fluoride ].

0017]As for said solid electrolyte powder, it is desirable that they are oxide stock glass ceramics which have lithium ion conductivity.

0018]Said electrode active material A lithium manganese multiple oxide, manganese dioxide, Lithium nickel complex oxide, a lithium cobalt multiple oxide, a lithium nickel cobalt multiple oxide, It is desirable to comprise any one sort of a lithium vanadium multiple oxide, a lithium titanium multiple oxide, titanium oxide, niobium oxide, vanadium oxide, tungstic oxide, or those derivatives or two or more sorts.

0019]

Function]By containing solid electrolyte powder, polyvinylidene fluoride (PVdF), and N-methyl pyrrolidone (NMP), the polyvinylidene fluoride (PVdF) which became gel is considered to be in the state of carrying out the coat of solid electrolyte particles and the electrode active material particle. Furthermore, movement of a lithium ion only not only in traffic in the bulk commodities of an electrode active material and solid electrolyte powder, In order that ion may move in the inside of the polyvinylidene fluoride (PVdF) which is carrying out the coat of the particles, and the double layer formed in granular structure of N-methyl pyrrolidone (NMP), that from which electrochemical characteristics equivalent to an organic system electrolysis solution are acquired is conjectured.

0020]

Embodiment of the Invention]Hereafter, the embodiment of the lithium cell of this invention is described. Drawing 1 is a sectional view showing the example of composition of the lithium cell concerning this invention. in drawing 1 -- 1 -- as for an anode and 2b, the electrode of a couple and 2a of a negative electrode and 3 are [ a positive

ole collector and 5 ] negative pole collectors a solid electrolyte layer and 4 a package and 2.

0021]If airtightness can be held, the package 1 is not limited to construction material, for example, can use metal, such as a laminate material made from aluminum, nickel, and aluminum, or a shrink case.

0022]The positive pole collector 4 or the negative pole collector 5 is formed for current collection of the anode a or negative-electrode 2b, for example, metallic foils, such as aluminum (aluminum), nickel (nickel), and copper (Cu), can be used for it.

0023]The anode 2a comprises the powder of the end of positive-active-material complications, a solid electrolyte layer, and an identical material, and negative-electrode 2b comprises negative-electrode-active-material powder, a solid electrolyte layer, and the complications end of an identical material. A conducting agent and a binder are added by this anode 2a and negative-electrode 2b if needed. As an electrode active material used for this anode 2a and negative-electrode 2b, For example, a lithium manganese multiple oxide, manganese dioxide, lithium nickel complex oxide, A lithium cobalt multiple oxide, a lithium nickel cobalt multiple oxide, a lithium vanadium multiple oxide, a lithium titanium multiple oxide, titanium oxide, niobium oxide, vanadium oxide, tungstic oxide, etc. and those \*\*\*\*\* can be used. Here, what shows \*\*\*\* potential to an anode for what a clear distinction does not have in positive active material and negative electrode active material, compares the charge and discharge potential of two kinds of compounds, and shows electropositive potential can be used for a negative electrode, respectively, and the cell of arbitrary voltage can be constituted.

0024]As the solid electrolyte layer 3, the anode 2a, or solid electrolyte powder mixed to negative-electrode 2b,  $0\text{Li}-41\text{Li}_2\text{O}-29\text{P}_2\text{O}_5$ ,  $40\text{Li}_2\text{O}-35\text{B}_2\text{O}_5-25\text{LiNbO}_3$ ,  $25\text{Li}_2\text{O}-25\text{aluminum}_2\text{O}_3-50\text{SiO}_2$ ,  $40\text{Li}_2\text{O}-6\text{Y}_2\text{O}_3-54\text{SiO}_2$ , or oxide stock noncrystalline solid electrolytes, such as  $65\text{LiNbO}_2-35\text{SiO}_2$ , and  $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  (here -- M -- aluminum.) Sc, Y, La,  $\text{Li}_{1+x}\text{Ti}_{2-x}(\text{PO}_4)_3$ , Oxide stock glass ceramics, such as  $\text{Li}_{0.5-3x}\text{R}_{0.5+x}\text{TiO}_3$  (R is La, Pr, Nd, and Sm here) and  $\text{Li}_{1+x+y}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ , are mentioned. As for the viewpoint of ionic conductivity to solid electrolyte powder, it is desirable here that they are oxide stock glass ceramics.

0025]If it is generally used to a lithium ion battery as a conducting agent, acetylene black, black lead, Ketchen black, etc. will be mentioned satisfactorily.

0026]As a binder, although polyvinylidene fluoride (PVdF), polytetrafluoroethylene (PTFE), polyolefines, polyimide, etc. are raised, from a viewpoint of reduction of the interfacial resistance between particles, it is desirable that it is POFUTSU-ized vinylidene (PVdF).

0027]The anode 2a or negative-electrode 2b mixes the powder of active material powder, a solid electrolyte, and an identical material so that it may become a rate of 50:50 to 97:3 by a volume ratio. When a solid electrolyte will be not less than 50% per volume, there is a problem to which the quantity of the electrode active material directly contributed to a charge-and-discharge reaction decreases too much, and electric capacity becomes small. Current will not flow becoming 3% or less per volume at all, and it stops functioning as a rechargeable battery. To this powder mixture, a conducting agent and polyvinylidene fluoride (PVdF) are mixed so that it may become a rate of 95-75:3-15:3-15 by a weight ratio. If a conducting agent and PVdF increase, and electric capacity will become small and will decrease too much, it will become difficult to maintain the firmness of an electrode active material and a solid electrolyte. Viscosity control is performed while adding and slurring N-methyl pyrrolidone (NMP) furthermore. It is more desirable to use for polyvinylidene fluoride (PVdF) what was dissolved in N-methyl pyrrolidone (NMP) a priori. The obtained slurry is carried out with \*\* on metallic foils, such as aluminum (aluminum), nickel (nickel), and copper (Cu), by the doctor blade method, casting method, or the roll coater method, and can be fabricated to a sheet shaped by drying N-methyl pyrrolidone (NMP).

0028]The solid electrolyte layer 3 mixes solid electrolyte powder and polyvinylidene fluoride (PVdF) so that it may become a rate of 97-75:25-3 by a weight ratio, and it performs viscosity control while it adds and slurs N-methyl pyrrolidone (NMP) further. Like the anode 2a and negative-electrode 2b, the molding method of the solid electrolyte layer 3 is a doctor blade method, casting method, or the roll coater method, and is acquired by laminating and drying on the anode 2a fabricated and dried previously or negative-electrode 2b.

0029]Even if it pressurizes by a roll press etc., it does not interfere, in order to raise the filling factor of an electrode active material or solid electrolyte powder.

0030]As long as the anode and/or the negative electrode comprise a mixture with the powder of the same material as a solid electrolyte, the lithium cell in which this invention is applied may be a primary battery, or may be a rechargeable battery. Cell shape is not limited to cylindrical, a square shape, a button type, a coin type, a flat type, etc.

0031]

Example][EXAMPLE] By mixing lithium hydroxide and manganese dioxide so that the mole ratio of Li and Mn may be set to 1:2, and carrying out heating calcination of this mixture at 900 °C in the atmosphere for 15 hours, the lithium manganese multiple oxide ( $\text{LiMn}_2\text{O}_4$ ) was compounded and this was made into positive active material.

Next, lithium hydroxide and manganese dioxide were mixed so that the mole ratio of Li and Mn might be set to 4:5, and carrying out heating calcination of this mixture at 600 °C in the atmosphere for 15 hours, the lithium manganese multiple oxide ( $\text{Li}_4\text{Mn}_5\text{O}_{12}$ ) was compounded and this was made into negative electrode active material.

0032]To each of this  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_4\text{Mn}_5\text{O}_{12}$ . As solid electrolyte powder, mix  $\text{Li}_{1+x+y}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$  so that it may become a rate of 8:2 by a volume ratio, and this powder mixture is received, Acetylene black and polyvinylidene fluoride (PVdF) were mixed so that it might become a rate of 82:8:10 by a weight ratio. What was beforehand dissolved in N-methyl pyrrolidone was used for polyvinylidene fluoride (PVdF). It was made to slur by adding 12g of polyvinylidene fluoride (PVdF) into this mixture, and furthermore, mixing into it. After carrying out this slurry with °C with a doctor blade method on aluminum (aluminum), polyvinylidene fluoride (PVdF) desiccation was carried out and it fabricated to the sheet shaped.

0033]The obtained sheet was pierced in quadrangle of 30 mm x 30 mm, and the with about 50 micrometers in thickness and a weight with °C of about 0.056 g anode 2a and negative-electrode 2b were obtained. The weight with °C turns into weight containing an electrode active material, acetylene black, and polyvinylidene fluoride (PVdF).

0034]Furthermore, to  $\text{Li}_{1+x+y}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ , polyvinylidene fluoride (PVdF) was mixed in the end of solid electrolyte complications so that it might become a rate of 9:1 by a weight ratio. Polyvinylidene fluoride (PVdF) used what was beforehand dissolved in N-methyl pyrrolidone (NMP) like the above-mentioned. It was made to slur by adding about 15g of N-methyl pyrrolidone (NMP) into this mixture, and furthermore, mixing into it. By laminating this slurry with °C and drying it on the above-mentioned anode, with a doctor blade method, the layered product of the anode 2a and the solid electrolyte 3 was obtained. The thickness of the solid electrolyte layer 3 laminated at this time was about 40 micrometers.

0035]With the obtained anode 2a and the layered product of the solid electrolyte layer 3, 0.3 cc, it dropped 0.2 cc of N-methyl pyrrolidone (NMP) at a time at negative-electrode 2b, and it was impregnated with it, respectively. Next, the anode 2a, the layered product of the solid electrolyte layer 3, and negative-electrode 2b which carried out being dropping impregnated of the N-methyl pyrrolidone (NMP) were piled up via the solid electrolyte layer 3, and the layered product of anode 2a-solid electrolyte layer 3-negative-electrode 2b was formed.

0036]The positive pole collector 4 was joined to the anode 2a of the layered product, and the negative pole collector 5 was similarly joined to negative-electrode 2b, and the lamination made from aluminum of the package was equipped. The lamination made from aluminum assembled the square-shaped lithium cell (35 mm x 35 mm) shown in drawing 1 by preparing two things cut in size of 35 mm x 35 mm, inserting the layered product which joined said charge collector, and bonding the peripheral part of the lamination made from aluminum by thermo-compression.

0037][Comparative example 1] The forming process of the synthesizing method of positive active material and negative electrode active material, an anode, and a negative electrode and the laminating method of the solid electrolyte layer were performed like the example. The anodes and negative electrodes which were obtained were about 52 micrometers in thickness, and about 0.059g in weight with °C.

0038]Although the layered product and negative electrode of an anode and a solid electrolyte which were dried were impregnated with N-methyl pyrrolidone (NMP) in the example, In this example, the layered product and negative electrode of an anode and a solid electrolyte which dried N-methyl pyrrolidone (NMP) were piled up like the example as it was, and the layered product of the anode-solid electrolyte layer-negative electrode was formed.

0039]Hereafter, the square-shaped lithium cell was assembled like the example.

0040][Comparative example 2] The synthesizing method of positive active material and negative electrode active material was performed like the example. Solid electrolyte powder was not mixed to an anode and a negative electrode, but it had composition of an electrode active material, acetylene black, and polyvinylidene fluoride (PVdF), and the mixture ratio was 82:8:10 in the weight ratio. The method of producing an anode and a negative electrode was performed like operation. The anodes and negative electrodes which were obtained were about 30

micrometers in thickness, and about 0.048g in weight with \*\*.

0041]It carried out being dropping impregnated of every 0.3 cc of the mixed solvents (PC:DME=1:1 volume ratio) of propylene carbonate (PC) and dimethoxyethane (DME) which dissolved  $\text{LiClO}_4$  in the anode and negative electrode which were obtained so that it might become concentration 1 M/l. Furthermore, the nonwoven fabric made from polypropylene was chosen as a separator, and this was impregnated with the same mixed solvent as the above-mentioned.

0042]The anode and negative electrode which were impregnated with the mixed solvent were piled up via the separator, and the layered product of the anode-solid electrolyte layer-negative electrode was formed.

0043]Hereafter, the square-shaped lithium cell was assembled like the example.

0044](Evaluation) The oxidation-reduction reaction was checked with the potentiostat (Hokuto Denko HAB-151) using the square-shaped lithium cell for evaluation obtained in this way. The measuring condition set the sweep rate of voltage to ten to 1 mV/sec, and the voltage range was set to 0-1.5V.

0045]As a result, the current accompanying the oxidation reduction which shows drawing 2 an example and shows drawing 3 the comparative example 2 was acquired. The current accompanying an oxidation-reduction reaction in an example was not checked.

0046]Drawing 2 and drawing 3 show the current which flows when voltage is impressed to a cell.

It is in such a good tendency that the flowing current is large.

In drawing 2 and drawing 3, the voltage of 0-0.5V is impressed continuously (cycle target), and plus side current and minus side current are flowing bordering on about 1 v. Plus side current is current accompanying oxidation reaction of an electrode.

Minus current is current accompanying a reduction reaction, and corresponds to charge and discharge, respectively.

0047]The lithium cell by this invention has the characteristic equivalent to the lithium cell which used the organic system electrolysis solution so that clearly from drawing 2 and drawing 3. With the composition which does not contain N-methyl pyrrolidone (NMP) like an example, from not being obtained the current accompanying an oxidation-reduction reaction. It is surmised that ion moved the polyvinylidene fluoride (PVdF) and the double layer formed in granular structure of N-methyl pyrrolidone (NMP) which exist not only in traffic in the bulk commodities of only an electrode active material and solid electrolyte powder but in the anode 2a, negative-electrode 2b, and the solid electrolyte layer 3.

0048]

Effect of the Invention]As mentioned above, the electrode of the couple which the lithium cell of this invention comprises with electrode active material powder, solid electrolyte powder, a conducting agent, and polyvinylidene fluoride, While electrochemical characteristics equivalent to the lithium cell using an organic system electrolysis solution by having allocated the solid electrolyte layer which comprises the solid electrolyte powder, polyvinylidene fluoride, and N-methyl pyrrolidone of an identical material between said electrodes are acquired, In the lithium cell by this invention, since the solvent and electrolyte salt which are conventionally used into the electrolyte are not included, the application range of a polymer electrolyte and a gel electrolyte can be extended further.

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EFFECT OF THE INVENTION

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TECHNICAL PROBLEM

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An electrolyte layer can be thin-film-ized and improvement in an energy density is expected.

Or since there are no worries about a liquid spill and corrosion and a volatile solvent is not used, that there is little danger of explosion or ignition etc. can desire improvement in a battery characteristic and safety.

0007]However, the above-mentioned polymer electrolyte has the problem that the degree of ion \*\*\*\* is low as compared with an organic system electrolysis solution, and since the gel electrolyte with which the polymer electrolyte was made to mix an organic system electrolysis solution has the ionic conductivity which is equal to in organic system electrolysis solution, development is performed briskly.

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functional group which can polymerize in JP,8-315855,A between two electrodes, and completing a polymerization after that, Generation of the interface between an electrolyte and an electrode is prevented and preventing exfoliation with a solid electrolyte and an electrode etc. is proposed.

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[0013]However, in these methods, there is a problem that electrolytic lithium ion conductivity will still become low, and current density will become small, and many the organic solvents and lithium salt which are main lithium ion conductors needed to be included.

[0014]In this invention, it is made in view of the above conventional problems, and the interfacial resistance of an electrode, a solid electrolyte layer and an electrode active material particle, solid electrolyte particles, electrode active material particles, and solid electrolyte particles is reduced.

Therefore, examination of various high molecular compounds and a solvent was performed for the purpose of finding out the electrochemical characteristics which are equal to an organic system electrolysis solution.

[0015]As a result, it differs from the gel electrolyte with which the conventional polymer electrolyte was made to mix an organic system electrolysis solution, If the combination of N-methyl pyrrolidone (NMP), the polyvinylidene fluoride (PVdF), and the solid electrolyte it was presupposed that electrolyte salt was not added and were not functioned as a solute of an electrolysis solution is used for an electrolyte, It found out acquiring electrochemical characteristics equivalent to the lithium cell using an organic system electrolysis solution, and resulted in this invention.

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[Translation done.]

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MEANS

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Means for Solving the Problem]In a lithium cell of this invention, a solid electrolyte layer which comprises this solid electrolyte powder, polyvinylidene fluoride, and N-methyl pyrrolidone is allocated in inter-electrode [ of a couple which comprises electrode active material powder solid electrolyte powder, a conducting agent, and polyvinylidene fluoride ].

[017]As for said solid electrolyte powder, it is desirable that they are oxide stock glass ceramics which have lithium ion conductivity.

[018]Said electrode active material A lithium manganese multiple oxide, manganese dioxide, Lithium nickel complex oxide, a lithium cobalt multiple oxide, a lithium nickel cobalt multiple oxide, It is desirable to comprise any one sort of a lithium vanadium multiple oxide, a lithium titanium multiple oxide, titanium oxide, niobium oxide, tantalum oxide, tungstic oxide, or those derivatives or two or more sorts.

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## OPERATION

[Function]By containing solid electrolyte powder, polyvinylidene fluoride (PVdF), and N-methyl pyrrolidone (NMP), the polyvinylidene fluoride (PVdF) which became gel is considered to be in the state of carrying out the coat of solid electrolyte particles and the electrode active material particle. Furthermore, movement of a lithium ion only not only in traffic in the bulk commodities of an electrode active material and solid electrolyte powder, In order that ion may move in the inside of the polyvinylidene fluoride (PVdF) which is carrying out the coat of the articles, and the double layer formed in granular structure of N-methyl pyrrolidone (NMP), that from which electrochemical characteristics equivalent to an organic system electrolysis solution are acquired is conjectured. [020]

[Embodiment of the Invention]Hereafter, the embodiment of the lithium cell of this invention is described. Drawing 1 is a sectional view showing the example of composition of the lithium cell concerning this invention. in drawing 1 - 1 -- as for an anode and 2b, the electrode of a couple and 2a of a negative electrode and 3 are [ a positive pole collector and 5 ] negative pole collectors a solid electrolyte layer and 4 a package and 2.

[021]If airtightness can be held, the package 1 is not limited to construction material, for example, can use metal, such as a laminate material made from aluminum, nickel, and aluminum, or a shrink case.

[022]The positive pole collector 4 or the negative pole collector 5 is formed for current collection of the anode or negative-electrode 2b, for example, metallic foils, such as aluminum (aluminum), nickel (nickel), and copper (Cu), can be used for it.

[023]The anode 2a comprises the powder of the end of positive-active-material complications, a solid electrolyte layer, and an identical material, and negative-electrode 2b comprises negative-electrode-active-material powder, a solid electrolyte layer, and the complications end of an identical material. A conducting agent and a binder are added by this anode 2a and negative-electrode 2b if needed. As an electrode active material used for this anode 2a and negative-electrode 2b, For example, a lithium manganese multiple oxide, manganese oxide, lithium nickel complex oxide, A lithium cobalt multiple oxide, a lithium nickel cobalt multiple oxide, a lithium vanadium multiple oxide, a lithium titanium multiple oxide, titanium oxide, niobium oxide, vanadium oxide, tungstic oxide, etc. and those \*\*\*\*\* can be used. Here, what shows \*\*\*\* potential to an anode for what a clear distinction does not have in positive active material and negative electrode active material, compares the charge and discharge potential of two kinds of compounds, and shows electropositive potential can be used for a negative electrode, respectively, and the cell of arbitrary voltage can be constituted.

[024]As the solid electrolyte layer 3, the anode 2a, or solid electrolyte powder mixed to negative-electrode 2b,  $0\text{LiI}-41\text{Li}_2\text{O}-29\text{P}_2\text{O}_5$ ,  $40\text{Li}_2\text{O}-35\text{B}_2\text{O}_5-25\text{LiNbO}_3$ ,  $25\text{Li}_2\text{O}-25\text{aluminum}_2\text{O}_3-50\text{SiO}_2$ ,  $40\text{Li}_2\text{O}-6\text{Y}_2\text{O}_3-54\text{SiO}_2$ , or oxide stock noncrystalline solid electrolytes, such as  $65\text{LiNbO}_2-35\text{SiO}_2$ , and  $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  (here -- M -- aluminum.) Sc, Y, La,  $\text{Li}_{1+x}\text{Ti}_{2-x}(\text{PO}_4)_3$ , Oxide stock glass ceramics, such as  $\text{Li}_{0.5-3x}\text{R}_{0.5+x}\text{TiO}_3$  (R is La, Pr, Nd, and Sm here) and  $\text{Li}_{1+x+y}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ , are mentioned. As for the viewpoint of ionic conductivity to solid electrolyte powder, it is desirable here that they are oxide stock glass ceramics.

[025]If it is generally used to a lithium ion battery as a conducting agent, acetylene black, black lead, Ketchen black, etc. will be mentioned satisfactorily.

[026]As a binder, although polyvinylidene fluoride (PVdF), polytetrafluoroethylene (PTFE), polyolefines, polyimide, etc. are raised, from a viewpoint of reduction of the interfacial resistance between particles, it is desirable that it : POFUTSU-ized vinylidene (PVdF).

[027]The anode 2a or negative-electrode 2b mixes the powder of active material powder, a solid electrolyte, and an identical material so that it may become a rate of 50:50 to 97:3 by a volume ratio. When a solid electrolyte will

ie not less than 50% per volume, there is a problem to which the quantity of the electrode active material directly contributed to a charge-and-discharge reaction decreases too much, and electric capacity becomes small. Current will not flow becoming 3% or less per volume at all, and it stops functioning as a rechargeable battery. To this powder mixture, a conducting agent and polyvinylidene fluoride (PVdF) are mixed so that it may become a rate of 95-75:3-15:3-15 by a weight ratio. If a conducting agent and PVdF increase, and electric capacity will become small and will decrease too much, it will become difficult to maintain the firmness of an electrode active material and a solid electrolyte. Viscosity control is performed while adding and slurring N-methyl pyrrolidone (NMP) furthermore. It is more desirable to use for polyvinylidene fluoride (PVdF) what was dissolved in N-methyl pyrrolidone (NMP) a priori. The obtained slurry is carried out with \*\* on metallic foils, such as aluminum (aluminum), nickel (nickel), and copper (Cu), by the doctor blade method, casting method, or the roll coater method, and can be fabricated to a sheet shaped by drying N-methyl pyrrolidone (NMP).

0028]The solid electrolyte layer 3 mixes solid electrolyte powder and polyvinylidene fluoride (PVdF) so that it may become a rate of 97-75:25-3 by a weight ratio, and it performs viscosity control while it adds and slurs N-methyl pyrrolidone (NMP) further. Like the anode 2a and negative-electrode 2b, the molding method of the solid electrolyte layer 3 is a doctor blade method, casting method, or the roll coater method, and is acquired by laminating and drying on the anode 2a fabricated and dried previously or negative-electrode 2b.

0029]Even if it pressurizes by a roll press etc., it does not interfere, in order to raise the filling factor of an electrode active material or solid electrolyte powder.

0030]As long as the anode and/or the negative electrode comprise a mixture with the powder of the same material as a solid electrolyte, the lithium cell in which this invention is applied may be a primary battery, or may be a rechargeable battery. Cell shape is not limited to cylindrical, a square shape, a button type, a coin type, a flat type, etc.

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DESCRIPTION OF DRAWINGS

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## Brief Description of the Drawings]

Drawing 1] It is a sectional view showing one embodiment of the lithium cell concerning this invention.

Drawing 2] It is a graph which shows the oxidation-reduction reaction concerning the example of this invention.

Drawing 3] It is a graph which shows the oxidation-reduction reaction concerning the comparative example of this invention.

## Description of Notations]

[ .... A negative electrode, 3 / .... A solid electrolyte layer, 4 / .... A positive pole collector, 5 / .... Negative pole collector ] .... A package, 2 .... The electrode of a couple, 2a .... An anode, 2b

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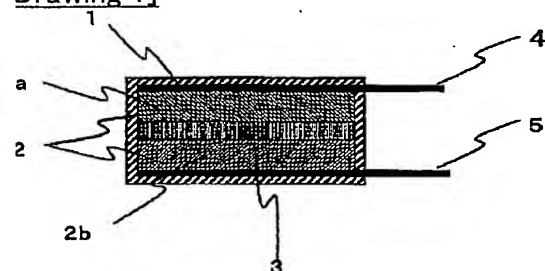
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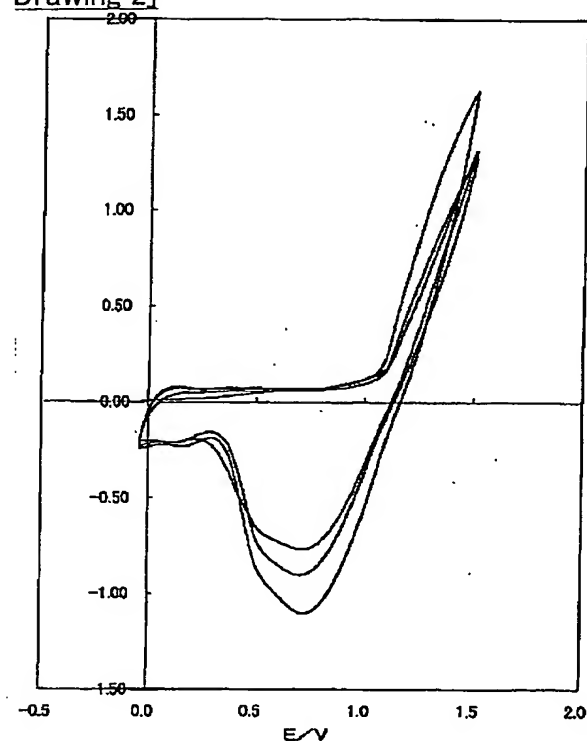
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## DRAWINGS

Drawing 1]

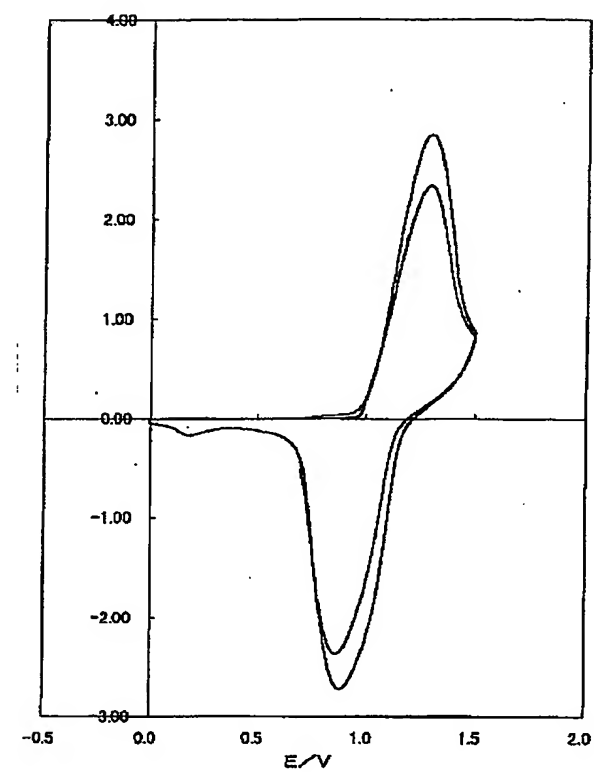


Drawing 2]



Drawing 3]





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